Chapter

Introductory Chapter: Structure-Processing-Properties Relationships in Stoichiometric and Nonstoichiometric Oxides

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1. Introduction

The research in the area of stoichiometric and nonstoichiometric compounds has grown considerably in the past decades forming an emerging scientific issue with a great impact in the materials science. According to the law of definite proportions, stoichiometric compounds (also referred to as daltonides) are chemical compounds in which atoms are combined in exact whole-number ratios. By contrast, nonstoichiometric compounds (also known as berthollides) are chemical compounds deviating from stoichiometry, and therefore their elemental composition cannot be represented by a ratio of well-defined natural numbers [1–4]. The nonstoichiometry occurs most often in solids due to defects in the lattice of their crystalline structures, and it is most common in the transition metal oxides, but also the group of nonstoichiometric compounds includes nitrides, fluorides, hydrides, carbides, metal sulfides, tellurides, and so on [2, 4–8].

The focus of the present book is on metal oxides, which present a large diversity of electrical, magnetic, optical, optoelectronic, thermal, electrochemical, and catalytic properties, making them suitable for a wide range of applications including sensors, solid-state electronic devices, thermoelectric power generation, and energy harvesting. This richness of properties is owed to the oxides' structure flexibility (especially of transition metal oxides) that makes them easily distort/adapt to the relative sizes of the ions forming the compound [9]. This implies a large chemical diversity providing for a complex interplay of intrinsic materials properties (related to the constituent elements) and extrinsic (defect-driven) properties (related to the presence of impurities and/or dopants).

Recent developments in the solid-state chemistry motivated by the prospect of new applications with topics such as colossal magnetoresistance, multiferroics, high-entropy stabilization, and superconductivity have uncovered rich complexities [10–21] that had not previously been recognized. These studies bring up some important issues that should be taken into account when the development of new multifunctional materials was intended.

The core focus that is implicit in most of today's studies in this field is firmly on the fundamental understanding of the *materials chemistry and microstructures and how they are related to the thermodynamic, electronic, and transport properties of stoichiometric and nonstoichiometric compounds.*

Several basic textbooks address this topic in relation to the defect chemistry and nonstoichiometry, many of them emphasizing on oxides [22–26].

Nonstoichiometric crystals were first interpreted, as regards their structure and their thermodynamics, in terms of the statistical thermodynamics of point defects [1, 2]. At small deviations from the stoichiometric composition, an approach assuming noninteracting and randomly distributed point defects was used [24]. In order to describe the higher deviations from stoichiometry, the interactions between the defect complexes, clustering, and long-range ordering into superstructures had to be taken into account [3], and extended defects structure models were developed. Particularly, in variable valence transition metal oxides, there is a strong coupling between defect structures, charge ordering, and orbital degrees of freedom that impacts property evolution. In fact, the transition from the point defect concept in highly dilute defect systems to extended defects models applicable in highly defective systems reflect the need to better define important phenomena in the real world and to determine to a large extend, the fundamental properties of a large range of advanced materials used in heterogeneous catalysis, fuel cells, sensors, oxygen and hydrogen separation membranes, battery materials, electrochromics and so on.

Searching for novel approaches and major breakthroughs in the materials properties, important factors that influence materials stoichiometry, e.g., the variation of the defect structure under controlled conditions (various kinds of doping, temperature, oxygen pressure), were excellently addressed in a series of books, papers, and reviews, and several key physicochemical descriptors (measured as well as calculated ones) showing a good correlation between stoichiometry, structure, and properties have been described [27–35].

Providing insights into new possibilities to control and optimize the properties based on the *correlation between the thermochemical stability, the preparation routes, and characterization* of different oxide-based compositions is also a topic that underpins the development of emergent devices and technology.

Besides the classical synthesis approaches based on high-temperature synthesis (solid-state reaction, thermal decomposition, high-temperature/high-pressure preparation) or on electrochemical methods (anodic electrocrystallization, direct current electrolysis), new materials synthesis techniques have evolved, such as mechanosynthesis, microwave hydrothermal synthesis, and atomic layer deposition [4]. In addition, advances in materials synthesis techniques, such as molecular beam epitaxy, reflection high-energy electron diffraction (RHEED)-assisted growth, ion implantation, or nanopatterning of defects by focused ion beams, allow the production of materials with controlled concentrations of point or planar defects and create interstitial doping and local strain fields that can enable patterning of circuits and magnetic domains [13, 36–43].

One of the challenging problems related to the understanding and practical exploitation of the enhanced properties of nanocrystalline materials is the thermal stabilization of a nanoscale grain size. The thermal stability of these microstructures is essential for adopting nanocrystalline materials in commercial processes and applications. Because the refinement in grain size is accompanied by a significant increase in volume fraction of grain boundaries, the thermal stability involves not only the stability of the grain structure, i.e., microstructure, but also the stability of the structure of the grain boundaries in nanocrystalline materials [44]. The lowering of interfacial energy with grain refinement and lattice strain in nanometer-sized crystallites plays an important role in controlling grain size stability during the grain growth in nanocrystalline phases [45, 46].

In parallel with the development of the synthesis methods, the characterization of different oxides based compositions is a crucial issue. It was argued that, due to the particularities of nonstoichiometric compounds, only after a thorough analysis of the composition, structure, and properties one can conclude that the compound

is a nonstoichiometric compound rather than a stoichiometric compound [4]. There is a complex task for which a combination of different methods is required. The results of the classical methods for the composition analysis, e.g., iodometry, cerimetry or electroanalysis methods, should be correlated with the crystallographic structure and microstructure information coming from application of X-ray diffraction techniques, neutron diffraction, high-resolution electron microscopy (HRTEM), laser Raman spectroscopy (LRS) and electron paramagnetic resonance (EPR), together other advanced technique imaging at the atomic level and allowing a detailed study of local defect structures and chemistry, e.g., scanning transmission electron microscopy (STEM) and in situ electron energy loss spectroscopy (EELS) [47–52]. In addition, many advances have come by measuring the physical properties such as electrical conductivity, magnetic, optical, and optoelectronic properties that strongly depend on stoichiometry and on types and concentration of the defects.

The oxide microstructure modification by using different synthetic methods and the modification of various compositional variables such as the nature and concentration of donor- or acceptor-type dopants are essential for obtaining optimum electrical and transport characteristics. Heat treatment is also an important step not only to ensure stability but also to control structural defects and grain size, also contributing to sensitivity and selectivity of the new materials. Previous reports on the substituted perovskites indicate that the mismatch at the A and B sites in the ABO_3 structure creates strain on grain boundaries which affect not only the electrical but also the thermodynamic properties [9], phase stability, and oxygen stoichiometry [53, 54]. It was also pointed out that the remarkable behavior of the multiferroic and magnetoresistive materials, as well as of the mixed ionic-electronic conducting ceramic membranes obtained by substitution of A and B sites, could be explained not only qualitatively by the structural changes upon doping but also by the fact that the thermodynamic properties are extremely sensitive to the chemical defects in oxygen sites [55–57]. An interesting relationship between the energetics of growth film conditions and the subsequent materials properties was observed when the pulsed laser deposition (PLD) was used in the synthesis of complex oxide films. Variations in the energetics of growth process can enable fine-tuning and control stoichiometry, dielectric response, thermal and electrical conductivity of films and heterointerfaces [58, 59].

The role of the energetic parameters in understanding the physical- and chemical-modified properties associated with the rise of the surface/volume ratio at a nanometer scale is also a topic of paramount importance [60]. Shifts in thermodynamics at the nanoscale and the strong interplay between the thermodynamic properties and electrical and structural characteristics in the hydrothermally prepared perovskite materials have been revealed [61]. In addition, at the nanometric scale, a large variety of morphologies and related surface properties can exist for the same metal oxide. This means that a great deal of attention must be turned to the energetic parameters which play an important role in the overall properties and behavior of materials. Exploring the relationships between morphology and thermodynamic properties of nanocrystalline $BaTiO_3$, it was shown that the enhancement of the dielectric properties for the $BaTiO_3$ hydrothermal-prepared powders with 1D morphology, comparatively with nanocubes or hollow-type morphologies, is strongly correlated with the increase in the binding energy of oxygen in the perovskite structure [62, 63].

Computational approaches, such as DFT-based calculations, phase-field modeling, molecular dynamics (MD) and Monte Carlo simulations) integrated at different stages of materials development have demonstrated to be important tools to address the complexity of based oxides stoichiometric and nonstoichiometric

compounds and provide information on phase competition and stability, defect dynamics and kinetics and so on. Thermodynamic Databases, such as CALPHAD (CALculation of PHAse Diagrams) or Databases including high-throughput DFT calculations, read-across and QSAR approaches, together with machine learning platforms have been developed contributing to the prioritization and screening of materials properties for applications as electronics, fuel cells, multiferroics, piezoelectrics, magnetocalorics, thermoelectrics [51, 64–73].

Critical advances in discovery and design of next-generation materials are expected by applying *the concept of the Materials Genome Initiative (MGI)* [74, 75] that tightly integrates high-throughput experiment (including both synthesis and characterization), theory, and computation. The development of advanced materials by using emerging synthetic and processing approaches should be based on the understanding of all factors affecting the reliability of these materials for specific applications (including a thorough thermodynamic analysis). The development of robust experimental methods to quantify microstructure and interfaces and to identify descriptors that strongly correlate with rearrangement dynamics on multiple lengthscales is also necessary. Multiscale and lifetime modeling should be accompanied by designing new tools and data analytics enabling high-content analysis and automated data evaluation and thus increasing the ability to understand and tailor the physical properties of materials. The strong interplay between these components offers great opportunities to establish support at the different tiered workflows directed toward emergent applications.

Driven by this concept, we have chosen in this book to concentrate on a limited number of chemical systems that exemplify the complex bridging between materials structure, synthesis, and properties. A special focus is on the role of thermodynamic parameters on the stabilization of the phase and physical properties in oxides. Various methods of synthesis are employed, each of these methods leaving their own mark on the properties of the resulting materials. The strong structure-processing-property relationship is emphasized in each of the chapters of this book, as can be seen from the brief overview of the main topics developed in these chapters: (i) The synthesis and complex characterization of a transitional metal oxide extensively used in industry, e.g., nickel oxide, are discussed. The understanding of the conditions of synthesis effect on the degree of nonstoichiometry provides clues for controlling the properties evolution. (ii) The stoichiometry and nonstoichiometry from crystal structure point of view are introduced along with some examples relevant for the importance of nonstoichiometry in the application-oriented research. Several advanced techniques available to ascertain stoichiometry are presented with a special emphasis on neutron diffraction techniques. Finally, important results obtained using neutron diffraction and scattering in identifying the structural modification which leads to superconductivity in the compounds are described. (iii) Particular aspects of the thermodynamic concepts related to associated phase equilibria in oxides exhibiting variable stoichiometry are emphasized. Insights into the equilibrium studies and construction of thermodynamic models of nonstoichiometric phases with application in high temperature superconducting materials are providing. (iv) The scientific and technological importance of the stoichiometry variation in the lead-free perovskite-structure materials, such as $SrTiO_3$ (ST) and $KTaO_3$ (KT), pure or modified, are defined. The strong relationship between the grain growth, the Sr/Ti or K/Ta ratio, the phase structure, morphology and dielectric response of ST and KT ceramics is overviewed. (v) The strong correlation between structure, nonstoichiometry and thermodynamic properties of some mixed conducting perovskite-type oxides $Ba_xSr_{1-x}Co_{1-y}Fe_yO_{3-\delta}$ (BSCF) studied as potential high-performance solid oxide fuel cells cathode materials is discussed and the effect of A- and B-site dopants concentration and of the

oxygen stoichiometry change on the thermodynamic stability and morphology of the BSCF samples was evidenced.

We hope the approach adopted on this book would give an account about the significance of the structure-processing-property relationship in stoichiometric and nonstoichiometric compounds as an important issue for both scientific and applicative reasons.

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References

[1] Anderson JS. Defect chemistry and non-stoichiometric compounds. In: Rao CNR, editor. Modern Aspects of Solid State Chemistry. Boston, MA: Springer; 1970. DOI: 10.1007/978-1-4684-1875-0_3

[2] Anderson JS. Nonstoichiometric compounds: A critique of current structural views. Proceedings - Indian Academy of Sciences, Chemical Sciences. 1984;**93**:861-904. DOI: 10.1007/BF02840335

[3] Collongues R. Nonstoichiometry in oxides. Progress in Crystal Growth and Characterization of Materials. 1992;**25**(4):203-240. DOI: 10.1016/0960-8974(92)90013-G

[4] Zhang JL, Hong GY. Nonstoichiometric compounds. In: Ruren X, Yan X, editors. Modern Inorganic Synthetic Chemistry. 2nd ed. Elsevier; 2017. pp. 329-354. DOI: 10.1016/B978-0-444-63591-4.00013-6

[5] Rao CNR. Transition metal oxides. Annual Review of Physical Chemistry. 1989;**40**:291-326. DOI: 10.1146/annurev.pc.40.100189.001451

[6] Lipatnikov VN, Zueva LV, Gusev AI, Kottar A. Disorder-order phase transformations and electrical resistivity of nonstoichiometric titanium carbide. Physics of the Solid State. 1998;**40**:1211-1218. DOI: 10.1134/1.1130523

[7] Gusev AI. Order-disorder transformations and phase equilibria in strongly nonstoichiometric compounds. Uspekhi Fizicheskikh Nauk. 2000;**170**:3-37. DOI: 10.1070/PU2000v043n01ABEH000647

[8] Rempel AA. Nonstoichiometric transition metal compounds. A review. In: Proceedings of the 17th Israeli-Russian Bi-National Workshop; 2018. pp. 167-189

[9] Stølen S, Bakken E, Mohn CE. Oxygen-deficient perovskites: Linking structure, energetics and ion Transport. Physical Chemistry Chemical Physics. 2006;**8**:429-447. DOI: 10.1039/b512271f

[10] Coey JMD, Viret M, von Molnar S. Magnetoresistance effect. Advances of Physics. 1999;**48**:167. DOI: 10.1080/00018730903363184

[11] Dabrowski B, Kolesnik S, Chmaissem O, Bukowski Z, Mais J, Kimball CW, et al. Spectacular magneto-related properties of complex oxides. In: Gibbs MRJ, editor. Modern Trends in Magnetostriction Study and Application. NATO Science Series (Series II: Mathematics, Physics and Chemistry), Vol. 5. Dordrecht: Springer; 2001. DOI: 10.1007/978-94-010-0959-1_10

[12] Tokura Y. Critical features of colossal magnetoresistive manganites. Reports on Progress in Physics. 2006;**69**:797-851. DOI: 10.1088/0034-4885/69/3/R06

[13] Mundy J, Brooks C, Holtz M, Moyer Jarrett A, Das H, Rébola AF, et al. Atomically engineered ferroic layers yield a room-temperature magneto electric multiferroic. Nature. 2016;**537**:523-527. DOI: 10.1038/nature19343

[14] Rost CM, Sachet E, Borman T, Moballegh A, Dickey EC, Hou D, et al. Entropy-stabilized oxides. Nature Communications. 2015;**6**:8485. DOI: 10.1038/ncomms9485

[15] Bérardan D, Franger S, Dragoe D, Meena AK, Dragoe N. Colossal dielectric constant in high entropy oxides. Physica Status Solidi. 2016;**10**(4):328-333. DOI: 10.1002/pssr.201600043

[16] Berardan D, Meena AK, Franger S, Herrero C, Dragoe N. Controlled

Jahn-Teller distortion in (MgCoNiCuZn) O-based high entropy oxides. Journal of Alloys and Compounds. 2017;**704**:693-700

[17] Jaing S, Hu T, Gild J, Zhou N, Nie J, Qin M, et al. A new class of high-entropy perovskite oxides. Scripta Materialia. 2018;**142**:116-120. DOI: 10.1016/j.scriptamat.2017.08.040

[18] Dragoe N, Bérardan D. Entropy stabilization provides a new direction for developing functional materials. Science. 2019;**366**(6465):573-574. DOI: 10.1126/science.aaz1598rapid.com

[19] Osenciat N, Bérardan D, Dragoe D, Leridon B, Holé S, Meena AK, et al. Charge compensation mechanisms in Li-substituted high-entropy oxides and influence on Li superionic conductivity. Journal of the American Ceramic Society. 2019;**102**:6156-6162. DOI: 10.1111/jace.16511

[20] Matin MA, Hossain MN, Ali MA, Hakim MA, Islam MF. Enhanced dielectric properties of prospective Bi0.85Gd0.15Fe_1-x$Cr_x$$O_3$ multiferroics. Results in Physics. 2019;**12**:1653-1659 DOI: 10.1016/j.rinp.2019.01.079

[21] Witte R, Sarkar A, Kruk R, Eggert B, Brand RA, Wende H, et al. High-entropy oxides: An emerging prospect for magnetic rare-earth transition metal perovskites. Physical Review Materials. 2019;**3**:034406

[22] Wagner C. Über den Mechanismus der elektrischen Stromleitung in Nernststift. Die Naturwissenschaften. 1943;**31**:265-268

[23] Kofstad P. Nonstoichiometry, Diffusion and Electrical Conductivity in Binary Metal Oxides. New York, London, Sydney, Toronto: Wiley-Interscience; 1972. DOI: 10.1002/maco.19740251027

[24] Kröger FA. Chemistry of Imperfect Crystals. Amsterdam: North-Holland Publishing Company; 1964. (OCoLC) 610606600

[25] Sørensen OT, editor. Non-stoichiometric Oxides. Academic Press; 1981. p. 441. DOI: 10.1016/B978-0-12-655280-5. X5001-9

[26] Kosuge K. Chemistry of Non-stoichiometric Compounds. USA: Oxford Press; 1994. DOI: 10.1021/ja945020d

[27] Centi G. Role of non-stoichiometry and soft chemistry in the preparation of advanced catalysts. Defect and Diffusion Forum. 2001;**191**:17-34. DOI: 10.4028/www.scientific.net/DDF.191.17

[28] Søgaard M, Hendriksen PV, Poulsen FW. Determination of transport and catalytic properties of mixed ionic and electronic conductors using transient responses. In: Linderoth S et al., editors. Solid State Electrochemistry. Proceedings of the Risø International Symposium on Materials Science; Risø (DK); 4-8 September 2005. Roskilde: Risø National Laboratory; 2005. pp. 355-362

[29] Hendriksen PV, Larsen PH, Mogensen M, Poulsen FW, Wiik K. Prospects and problems of dense oxygen permeable membranes. Catalysis Today. 2000;**56**:283-295. DOI: 10.1016/S0920-5861(99)00286-2

[30] Hashimoto SI, Kammer Hansen K, Larsen PH, Poulsen FW, Mogensen M. A study of $Pr_{0.7}Sr_{0.3}Fe_{1-x}Ni_xO_{3-\delta}$ as a cathode material for SOFCs with intermediate operating temperature. Solid State Ionics. 2005;**176**:1013-1020. DOI: 10.1016/j.ssi.2004.09.010

[31] Sun G, Thygesen A, Ale MT, Mensah M, Poulsen FW, Meyer AS. The significance of the initiation process parameters and reactor design for maximizing the efficiency of microbial fuel cells. Applied Microbiology and Biotechnology. 2014;**98**:2415-2427. DOI: 10.1007/s00253-013-5486-5

[32] Ovtar S, Søgaard M, Norrman K, Hendriksen PV. Oxygen Exchange and Transport in $(La_{0.6}Sr_{0.4})_{0.98}FeO_{3-d}$–$Ce_{0.9}Gd_{0.1}O_{1.95}$ Dual-Phase Composites. Journal of the Electrochemical Society. 2018;**165**(3):F220-F231. DOI: 10.1149/2.1031803jes

[33] Fergus JW. Oxide materials for high temperature thermoelectric energy conversion. Journal of the European Ceramic Society. 2012;**32**:525-540. DOI: 10.1016/j.jeurceramsoc.2011.10.007

[34] Somani PR, Radhakrishnan S. Electrochromic materials and devices: Present and future. Materials Chemistry and Physics. 2002;**77**:117-133. DOI: 10.1016/S0254-0584(01)00575-2

[35] Llordés A, Wang Y, Fernandez-Martinez A, Xiao P, Lee T, Poulain A, et al. Linear topology in amorphous metal oxide electrochromic networks obtained via low-temperature solution processing. Nature Materials. 2016;**15**:1267-1273. DOI: 10.1038/nmat4734

[36] Xu RR, Pang WQ. Inorganic Synthesis and Preparation Chemistry. Beijing: Higher Education Press; 2001. p. 44

[37] Takamura Y, Chopdekar RV, Scholl A, Doran A, Liddle JA, Harteneck B, et al. Tuning magnetic domain structure in nanoscale $La_{0.7}Sr_{0.3}MnO_3$ islands. Nano Letters. 2006;**6**(6):1287-1291. DOI: 10.1021/nl060615f

[38] Lee C, Orloff N, Birol T, Zhu Y, Goian V, Rocas E, et al. Exploiting dimensionality and defect mitigation to create tunable microwave dielectrics. Nature. 2013;**502**:532-536. DOI: 10.1038/nature12582

[39] Mathew S, Annadi A, Chan TK, Asmara TC, Zhan D, Wang XR, et al. Tuning the interface conductivity of $LaAlO_3/SrTiO_3$ using ion beams: Implications for patterning. ACS Nano. 2013;**7**(12):10572-10581. DOI: 10.1021/nn4028135

[40] Yang Y, Liu XL, Yang Y, Xiao W, Li ZW, Xue DS, et al. Synthesis of nonstoichiometric zinc ferrite nanoparticles with extraordinary room temperature magnetism and their diverse applications. Journal of Materials Chemistry C. 2013;**1**(16):2875-2885. DOI: 10.1039/C3TC00790A

[41] Saremi S, Dedon LR, Mundy JA, Hsu SL, Chen Z, Damodaran AR, et al. Enhanced electrical resistivity and properties via ion bombardment of ferroelectric thin films. Advanced Materials. 2016;**28**:10750-10756. DOI: 10.1002/adma.201603968

[42] Damodaran AR, Breckenfeld E, Chen Z, Lee S, Martin LW. Enhancement of ferroelectric Curie temperature in $BaTiO_3$ films via strain induced defect dipole alignment. Advanced Materials. 2014;**26**:6341-6347. DOI: 10.1002/adma.201400254

[43] Saremi S, Gao R, Dasgupta A, Martin LW. New facets for the role of defects in ceramics. American Ceramic Society Bulletin. 2018;**97**(1):16-23

[44] Koch CC. Processing structure property relationships in ultrafine grain and nanocrystalline materials. JPCS. 2009;**144**:1-8. DOI: 10.1088/1742-6596/144/1/012081

[45] Murty BS, Datta MK, Pabi SK. Structure and thermal stability of nanocrystalline materials. Sadhana. 2003;**28**:23-45. DOI: 10.1007/BF02717124

[46] Gleiter H. Nanostructured materials: Basic concepts and microstructure. Acta Materialia. 2000;**48**:1-29. DOI: 10.1016/S1359-6454(99)00285-2

[47] Xu W, Bowes PC, Grimley ED, Irving DL, Le Beau JM. In-situ realspace

imaging of single crystal surface reconstructions via electron microscopy. Applied Physics Letters. 2016;**109**:201601. DOI: 10.1063/1.4967978

[48] Seebauer EG, Kratzer MC. Experimental and computational characterization. In: Charged Semiconductor Defects: Structure, Thermodynamics and Diffusion. London: Springer; 2009. pp. 39-61. DOI: 10.1007/978-1-84882-059-3

[49] Karppinen M, Yamauchi H. Chemical design of copper-oxide superconductors: Homologous series and oxygen engineering in frontiers. In: Narlikar AV, editor. Superconducting Materials. Berlin: Springer Verlag; 2005. pp. 255-294

[50] Yadav AK, Nelson CT, Hsu SL, Hong Z, Clarkson JD, Schlepütz CM, et al. Observation of polar vortices in oxide superlattices. Nature. 2016;**530**:198-201. DOI: 10.1038/nature16463

[51] Bartel CJ, Sutton C, Goldsmith BR, Ouyang R, Musgrave CB, Ghiringhelli LM, et al. New tolerance factor to predict the stability of perovskite oxides and halides. Science Advances. 2019;**5**(2):eaav0693. DOI: 10.1126/sciadv.aav0693

[52] Itahashi YM, Ideue T, Saito Y, Shimizu S, Ouchi T, Nojima T, et al. Nonreciprocal transport in gate-induced polar superconductor $SrTiO_3$. Science Advances. 2020;**6**(13):eaay9120. DOI: 10.1126/sciadv.aay9120

[53] McIntosh S, Vente JF, Haije WG, Blank DHA, Bouwmeester HJM. Phase stability and oxygen non-stoichiometry of SrCo0.8Fe0.2O3−δ measured by in situ neutron diffraction. Solid State Ionics. 2006;**177**:833-842. DOI: 10.1016/j.ssi.2006.02.017

[54] Kuhn M, Kim JJ, Bishop SR, Tuller HL. Oxygen nonstoichiometry and defect chemistry of perovskite-structured $Ba_xSr_{1-x}Ti_{1-y}Fe_yO_{3-y/2+\delta}$ solid solutions. Chemistry of Materials. 2013;**25**:2970-2975. DOI: 10.1021/cm400546z

[55] Tanasescu S, Petcu A, Ianculescu A. Chapter 15: Effects of doping and nonstoichiometry on the thermodynamic properties of multiferroic ceramics. In: Lallart M, editor. Ferroelectrics—Vol. II. Rijeka, Croatia: InTech; 2011. pp. 347-372. DOI: 10.5772/16392

[56] Tanasescu S, Maxim F, Teodorescu F, Giurgiu LM. Influence of composition and particle size on spin dynamics and thermodynamic properties of magnetoresistive perovskites. Journal of Nanoscience and Nanotechnology. 2008;**8**(2):914-923. DOI: 10.1166/jnn.2008.D127

[57] Tanasescu S, Yáng Z, Martynczuk J, Teodorescu F, Botea A, Totir N, et al. Effects of A-site composition and oxygen nonstoichiometry on the thermodynamic stability of compounds in the Ba-Sr-Co-Fe-O system. Solid State Chemistry. 2013;**200**:354-362. DOI: 10.1016/j.jssc.2013.01.030

[58] Breckenfeld E, Wilson R, Karthik J, Damodaran AR, Cahill DG, Martin LW. Effect of growth induced (non)stoichiometry on the structure, dielectric response, and thermal conductivity of $SrTiO_3$ thin films. Chemistry of Materials. 2012;**24**:331. DOI: 10.1021/cm203042q

[59] Breckenfeld E, Bronn N, Mason N, Martin LW. Tunability of conduction at the $LaAlO_3/SrTiO_3$ heterointerface: Thickness and compositional studies. Applied Physics Letters. 2014;**105**:121610. DOI: 10.1063/1.4896778

[60] Navrotsky A, Ma C, Lilova K, Birkner N. Nanophase transition metal oxides show large thermodynamically

driven shifts in oxidation-reduction equilibria. Science. 2010;**330**:199. DOI: 10.1126/science.1195875

[61] Rusti CF, Badilita V, Sofronia AM, Taloi D, Anghel EM, Maxim F, et al. Thermodynamic properties of $Ba_{0.75}Sr_{0.25}TiO_3$ nanopowders obtained by hydrothermal synthesis. Journal of Alloys and Compounds. 2017;**693**:1000-1010. DOI: 10.1016/j.jallcom.2016.09.215

[62] Maxim F, Poenaru I, Teodorescu F, Tanasescu S. Barium titanate torus-like particles: Low-temperature synthesis and formation mechanism. European Journal of Inorganic Chemistry. 2014;**30**:5160-5167. DOI: 10.1002/ejic.201402497

[63] Maxim F, Berger D, Teodorescu F, Hornoiu C, Lete C, Tanasescu T. Low-temperature synthesis and thermodynamic and electrical properties of barium Titanate Nanorods. Journal of Nanomaterials. 2015;**1**:1-10. DOI: 10.1155/2015/827641

[64] Olson GB. Designing a new material world. Science. 2000;**288**:993-998

[65] Greeley J, Jaramillo T, Bonde J, Chorkendorff I, Nørskov JK. Computational high-throughput screening of electrocatalytic materials for hydrogen evolution. Nature Materials. 2006;**5**:909-913. DOI: 10.1038/nmat1752

[66] Poulsen FW. Methods and limitations in defect chemistry modelling [Thesis]. Roskilde, Denmark: Risø National Laboratory, DTU; 2007

[67] National Research Council. Integrated Computational Materials Engineering: A Transformational Discipline for Improved Competitiveness and National Security. Washington, DC: The National Academies Press; 2008. p. 152

[68] Kattner UR, Campbell CE. Invited review: Modelling of thermodynamics and diffusion in multicomponent systems. Materials Science and Technology. 2009;**25**:25443-25459. DOI: 10.1179/17432840837200

[69] Roy A, Benntt JW, Rabe K, Vanderbilt D. Half-heusler semiconductors as piezoelectrics. Physical Review Letters. 2012;**109**(3):037602. DOI: 10.1103/PhysRevLett.109.037602

[70] Curtarolo S, Hart GL, Nardelli MB, Mingo N, Sanvito S, Levy O. The high-throughput high way to computational materials design. Nature Materials. 2013;**12**(3):191-201. DOI: 10.1038/nmat3568

[71] Marzari N. Materials modelling: The frontiers and the challenges. Nature Materials. 2016;**15**:381-382. DOI: 10.1038/nmat4613

[72] Montoya J, Seitz L, Chakthranont P, Vojvodic A, Jaramillo TF, Nørskov JK. Materials for solar fuels and chemicals. Nature Materials. 2016;**16**:70-81. DOI: 10.1038/nmat4778

[73] Jain A, Shin Y, Persson KA. Computational predictions of energy materials using density functional theory. Nature Reviews Materials. 2016;**1**:15004. DOI: 10.1038/natrevmats.2015.4

[74] de Pablo JJ, Jones B, Kovacs CL, Ramirez AP. The materials genome initiative, the interplay of experiment, theory and computation. Current Opinion in Solid State & Materials Science. 2014;**18**:99-117. DOI: 10.1016/j.cossms.2014.02.003

[75] de Pablo JJ, Jackson NE, Webb MA, Chen LQ, Moore JE, Morgan D, et al. New frontiers for the materials genome initiative. Computational Materials. 2019;**5**:41. DOI: 10.1038/s41524-019-0173-4